



Selective separation of nickel and cadmium from sulfate solutions of spent nickel–cadmium batteries using mixtures of D2EHPA and Cyanex 302



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HIGHLIGHTS

- A separation of Cd and Ni from sulfate solutions using mixtures of D2EHPA and Cyanex 302 was achieved.
- Extraction reactions of Cd were investigated and thermodynamic parameters were calculated.
- Distribution coefficients of Cd were discovered and it was in good agreement with the experimental values.

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ABSTRACT

The synergistic effect of Cyanex 302 on solvent extraction of nickel and cadmium from sulfate solution with D2EHPA diluted in kerosene has been investigated with the aim of increasing separation efficiency. Experiments are carried out using the sole D2EHPA and also D2EHPA–Cyanex 302 mixtures in different ratios. As a result, satisfactory separation has been found with a Cyanex 302 to D2EHPA ratio of 0.1 M:0.5 M. The extraction equilibrium constants, enthalpy change, and entropy change of the cadmium extraction are also determined. The stoichiometric coefficient of cadmium for the sole D2EHPA and three different D2EHPA to Cyanex 302 ratios has been determined by applying the slope analysis method. The experimental data of cadmium extraction have been employed to model the distribution coefficient of cadmium by multiple linear regression.

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1. Introduction

Today, rechargeable batteries are widely used as a portable power source in almost every electronic device. Ni–Cd batteries are one of the most common rechargeable batteries which are manufactured in two main groups of small consumer cells and large industrial batteries with approximately 80% being used in consumer products. Ni–Cd cells have various applications such as cordless electric utensils, cordless telephones, airplane engine starters, and communicational distribution systems [1].

Since nickel and cadmium are heavy metals and they are considered as suspected carcinogens, depleted Ni–Cd batteries are classified as hazardous waste. Given the risk associated with uncontrolled disposal, directions for issuing legislation on disposal

and recycling of spent batteries have been made in industrialized countries [2]. Furthermore, recycling of Ni–Cd batteries is receiving increasing attention from both economic and environmental points of view. Different methods have been used for recycling these wastes through pyrometallurgical processes, such as the SAB NIFE, SNAM, and INMETCO [3–6]. In these processes, cadmium recovery are based on distillation at around 900 °C and it was shown that most of valuable heavy metals such as nickel and cobalt are not recycled very well [1]. Pyrometallurgical treatments are also energy-consuming and some of their by-products are consisted of dust and gases. Hence, different hydrometallurgical processes have been developed to solve the crisis of used batteries. The hydrometallurgical processes such as leaching and solvent extraction have been widely used in separation, purification, and recovery of metal ions from solid wastes and they are more economical and environmentally suitable to treat spent rechargeable batteries [7]. Several studies have been implemented on leaching and solvent

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Table 1
Properties of the solvents.

Characteristic	D2EHPA	Cyanex 302
Molecular formula	$C_{16}H_{35}O_4P$	$C_{16}H_{35}OPS$
Molecular Weight	322.4	306.5
Solubility in water ($g\ L^{-1}$)	<0.01	0.003
Density ($g\ cm^{-3}$)	0.970	0.930
Appearance	Colorless or yellowish, oily liquid	Pale yellow

extraction (SX) of spent Ni–Cd batteries. Leaching of spent batteries is usually done in sulfate or chloride media, while solvent extraction has been employed using different extractants. When H_2SO_4 is the leachant, organophosphorus extractants have been employed. Solvent extraction of cadmium from leach solutions has been studied by Cyanex 301 (bis(2,4,4 trimethylpentyl) dithiophosphinic acid) [1], D2EHPA (di-2-ethylhexyl phosphoric acid) [8,9], Cyanex 302 (bis(2,4,4-trimethylpentyl) monothiophosphinic acid) [10], Cyanex 923 (a mixture of four trialkyl-phosphine oxides ($R_3P=O$, $R_2R'P=O$, $R'_3P=O$, $R'_2RP=O$, where R = hexyl and R' = octyl)) [2,11], Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid), Tops 99 (an equivalent of di-2-ethylhexyl phosphoric acid) and PC 88A (2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester) [12]. Almela and Elizalde [10] analyzed the suitability of Cyanex 302 for extraction of Cadmium compared with other similar organophosphorus extractants, such as Cyanex 272. They found Cyanex 302 to be effective in extracting cadmium in very acidic conditions. Cadmium extraction with D2EHPA involves co-extraction of both Ni and Co [8], which causes issues in the separation process efficiency. Application of phosphorus based extractants for the solvent extraction studies of Ni such as TOPS 99 [13], D2EHPA [14], and Cyanex 272 [2,15] has also been investigated.

Instead of using a single extractant, mixtures of extractants can give rise to synergistic effects and better selectivity of metal extraction/separation in solvent extraction processes. Synergism was applied for the separation of nickel–cadmium species from sulfate solutions by Reddy et al. [16]. They reported that a mixture of TOPS 99 and Cyanex 471X performed a clear separation of cadmium from nickel in sulfate solutions. Addition of Cyanex 471X suppressed the co-extraction of Ni drastically from 2.03 to 0.28%, thereby allowing the separation of Cd more efficient with mixture of the extractants [16,17]. The synergistic effect of Cyanex 302 when mixed with D2EHPA has been previously used for separation of nickel and cobalt [18], zinc from iron (II) and (III) [19], and for the separation of zinc and manganese in sulfate media [20].

Although Cyanex 302 offers good separation of cadmium and nickel, it is relatively expensive to be used commercially. While D2EHPA is cheaper compared to other industrial organic solvents, its separation efficiency is unacceptable for this purpose. Therefore, for the commercial application purposes, we have examined in this research the synergistic potential of D2EHPA and Cyanex 302 mixtures for extraction and separation of Ni and Cd from sulfate media. Different ratios of D2EHPA and Cyanex 302 diluted in kerosene were employed as the organic phase. In addition, the extraction mechanism and thermodynamic parameters of cadmium for both single D2EHPA and the mixture of Cyanex 302 and D2EHPA were studied in detail.

2. Experimental

2.1. Materials

Cadmium sulfate (97% pure) and nickel sulfate (98% pure) salts were obtained from Merck, Germany. The organic solvents used in this work were industrial-grade di-(2-ethylhexyl) phosphoric acid (D2EHPA), 97% pure, from Bayer, Germany, and bis-(2,4,4-

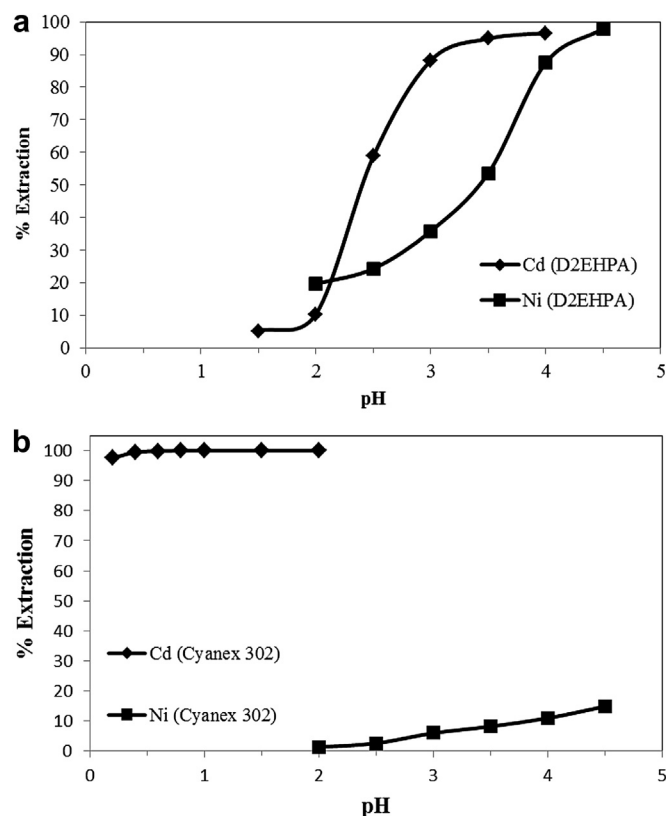


Fig. 1. a – Effect of equilibrium pH on extraction of cadmium and nickel using 0.6 M D2EHPA at 25 °C and A/O ratio of 1:1. b – Effect of equilibrium pH on extraction of cadmium and nickel using 0.6 M Cyanex 302 at 25 °C and A/O ratio of 1:1.

trimethylpentyl) monothiophosphinic acid (Cyanex 302), 98% pure, from Fluka, Canada. The properties of the solvents are illustrated in Table 1. The extractants were used without further purification. Kerosene (boiling range 160–200 °C, composed of aliphatic hydrocarbons), from Tehran Oil Refinery Co. was used as a diluent in the present work. Sulfuric acid (98% pure) and sodium hydroxide, from Merck, Germany, were used for pH adjustment.

2.2. Experimental procedure

Stock solution of nickel (II) and cadmium (II) with a concentration of $2\ g\ L^{-1}$ each was prepared by dissolving the required amount of nickel sulfate and cadmium sulfate in distilled water. Each extraction test was performed by mixing 200 mL of the aqueous phase solution with 200 mL of the organic phase containing 20% v/v of the extractant and 80% v/v kerosene. This aqueous to organic phase ratio (A/O) of 1:1 was used in all tests. The concentration of the extractant in the organic phase (sole D2EHPA or D2EHPA–Cyanex 302 mixtures) was 0.6 M. During mixing, temperature of the system was controlled by a thermostatic bath. Experiments were carried out at 25, 40 and 60 °C. A PY-11 pH meter (Sartorius, Germany) was used to monitor pH during the experiments. In order to obtain the extraction isotherms, the pH was successively changed by adding either sulfuric acid or sodium hydroxide solution at 10 M concentration drop wise while the two-phase mixture was being agitated via a mechanical stirrer. After the pH was stable, a sample was taken, transferred to a separatory funnel, and allowed to disengage. In all experiments, agitation time was at least 10 min to ensure that the equilibrium was attained (although equilibrium could be achieved in less than 10 min [14,21,22]).

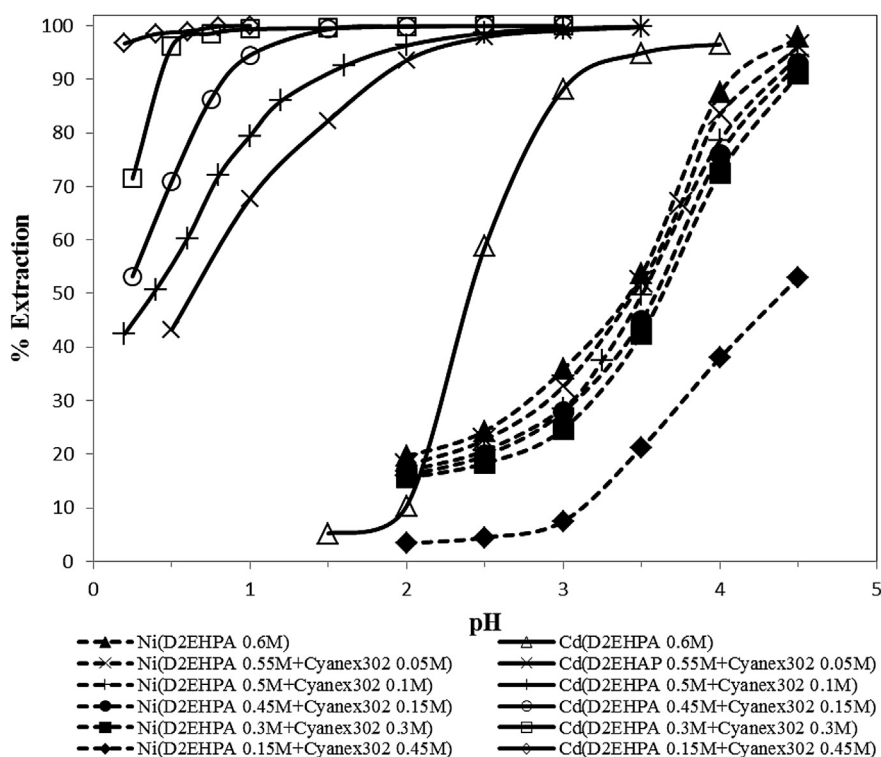


Fig. 2. Effect of additions of Cyanex 302 to D2EHPA on the extraction of Cd (II) and Ni (II) at 25 °C and A/O ratio of 1:1.

Nickel and cadmium concentration in the aqueous phase was obtained directly, after suitable dilutions, by atomic absorption spectroscopy (GBC, Avanta Σ). The concentration of metal ions in the organic phase was calculated from the difference between concentrations in the aqueous phase before and after extraction by mass balance.

The distribution ratio (D) was calculated as the ratio of concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium. From D values, the percentage extraction ($%E$) and separation factor (β) were calculated using Eq. (1).

$$%E = \frac{D \times 100}{D + (V_{aq}/V_{org})} \quad (1)$$

where V_{aq} and V_{org} are the volume of aqueous and organic phase, and Eq. (2):

$$\beta = \frac{D_{Ni}}{D_{Cd}} = \frac{[Ni]_{org}/[Ni]_{aq}}{[Cd]_{org}/[Cd]_{aq}} \quad (2)$$

3. Results and discussion

3.1. Effect of equilibrium pH

Initial experiments on the extraction of Ni and Cd from synthetic sulfate solutions were conducted in the equilibrium pH range 0.2–4.5 with individual extractants of 0.6 M D2EHPA as well as Cyanex 302 dissolved in kerosene. Fig. 1a illustrates the percentage of cadmium and nickel ions extracted as a function of equilibrium pH using 0.6 M D2EHPA diluted in kerosene at 25 °C. On the whole, increasing pH from 1.5 to 4 increases the extraction of both ions significantly. This is consistent with observations of Owusu et al.

[14] and Nogueira and Delmas [8]. As seen in Fig. 1, by increasing pH from 1.5 to 4.0, cadmium extraction increases from 5.2% to 96.6%. At equilibrium pH of 3.5, cadmium extraction was completed to higher than 95%. In the case of nickel, 35.9% of the ions were extracted at pH of 3.0, which is considerably lower than the 88% of cadmium extraction at this pH. The $pH_{0.5}$ values (the pH at 50% metal extraction) for nickel and cadmium were determined from the figure as 3.4 and 2.4, respectively. This indicates that cadmium is being extracted at a lower pH compared with that of nickel, when 0.6 M D2EHPA in kerosene is used. A similar behavior was reported by Nogueira and Delmas [8] where they examined nickel and cadmium extraction by 1 M D2EHPA diluted in Shell D70. The results also imply that cadmium extraction with D2EHPA involves co-extraction of nickel. Extraction of metals using 0.6 M Cyanex 302 showed systematic increase in the percentage extraction of Cd from 97 to 99.9% with increase in pH of aqueous phase from 0.2 to 2.0 (Fig. 1b). The percentage extraction of Ni started after an equilibrium pH of 2.5, where it was only 2.6% and the increase with the equilibrium pH was mild (14.8% at pH 4.5). This result is consistent with literature data [18,23].

To decrease the co-extraction of Ni and increase the selective extraction of Cd, mixed extractant systems consisting D2EHPA and Cyanex 302 in kerosene were applied. Fig. 2 shows the percentage of cadmium and nickel ions extracted as a function of pH at different D2EHPA to Cyanex 302 ratios at 25 °C. It illustrates significant synergistic shifts of cadmium and nickel isotherms due to the addition of Cyanex 302 to D2EHPA. As can be seen in the figure, by increasing the ratio of Cyanex 302 to D2EHPA, the cadmium extraction curve shifted more to the left and that of nickel to the right. In other words, addition of Cyanex 302 to D2EHPA significantly improves the separation of cadmium over nickel [24].

Values of the $\Delta pH_{0.5}$ (difference between $pH_{0.5}$ for cadmium and nickel) determined from extraction isotherms in Fig. 2, have been shown in Table 2. It is seen that $\Delta pH_{0.5}$ is significantly higher when

Table 2

Values of $pH_{0.5}$ for nickel and cadmium and $\Delta pH_{0.5}$ (Cd–Ni) for different mixtures of D2EHPA and Cyanex 302 at 25 °C.

Molar ratio of D2EHPA:Cyanex 302	$pH_{0.5}$		$\Delta pH_{0.5}$ (Cd–Ni)
	Cd	Ni	
0.6:0.0	2.4	3.4	1
0.55:0.05	0.7	3.5	2.8
0.5:0.1	0.4	3.5	3.1
0.45:0.15	<0.2	3.6	>3.4
0.3:0.3	<0.2	3.7	>3.5
0.15:0.45	<0	4.4	>4.4

using a mixture of Cyanex 302 and D2EHPA over the sole D2EHPA. Also, the most selective extraction results can be achieved by D2EHPA to Cyanex 302 volume ratio of 1:3 (0.15 M D2EHPA:0.45 M Cyanex 302) in which the $\Delta pH_{0.5}$ increases from 1 (for 0.6 M D2EHPA) to more than 4.4. Fig. 3 illustrates the effect of adding Cyanex 302 as synergist on $pH_{0.5}$. It is seen that adding Cyanex 302 to D2EHPA decreases $pH_{0.5}$ values of cadmium and increases those of nickel and as the result, $\Delta pH_{0.5}$ increases. It is worth mentioning that, increasing the amount of Cyanex 302 beyond 0.45 M has a negligible effect on the extraction efficiency. Moreover, since Cyanex 302 is more expensive than D2EHPA, increasing the amount of Cyanex 302 in the extractant mixture is not commercially favorable.

The separation factor value for cadmium and nickel ($\beta_{Cd/Ni}$) indicates how efficiently the extractant can separate nickel from cadmium. Table 3 illustrates the separation factors of various proportions of D2EHPA to Cyanex 302 at different pHs. The best separation factor of 2.83×10^5 was obtained for the mixture of 0.15 D2EHPA:0.45 Cyanex 302 at pH 2. It should be mentioned that at pH 3, approximately 100% of cadmium was extracted while nickel extraction was negligible and it was about 3%. At higher pH levels than 3, nickel extraction is increased and as the result, separation factor values are decreased.

To quantify the synergic effect, the synergistic coefficient (R) is defined as [25]: $R = D_{\text{mixture}}/D_{\text{Cyanex302}} + D_{\text{D2EHPA}}$, where D_{mixture} , $D_{\text{Cyanex302}}$ and D_{D2EHPA} are the distribution ratio of cadmium (or nickel) using the synergistic mixture and the individual Cyanex 302 and D2EHPA extractants, respectively. The calculated synergistic coefficients in the pH range of 2.0–3.0 are listed in Table 4. Whatever this coefficient is increased from 1, we could deduce that simultaneous effect of extractants lead to an increase in metal extraction in comparison with utilizing each extractant separately. The best condition will occur when the synergistic coefficient is higher than 1 and the $\Delta pH_{0.5}$ is maximum. Based on Table 4, synergistic coefficient of nickel and cadmium is reduced to less than 1, which means simultaneous utilizing of Cyanex 302 and D2EHPA decreases the extraction of both metals compared to the usage of each extractant separately. Nevertheless, the reduction is not significant and also causes an increase of $\Delta pH_{0.5}$ nickel and cadmium which was the aim of this investigation. From Table 4, it can be seen that R of cadmium increases with increasing pH and the ratio of Cyanex 302 to D2EHPA. Based on the results, it can be concluded that both increasing pH and Cyanex 302 to D2EHPA ratio will decrease synergistic coefficient of nickel.

3.2. Effect of temperature

To assess the effect of temperature, extraction-pH isotherms of cadmium and nickel at 40 and 60 °C were determined for a 0.5 M:0.1 M mixture of D2EHPA:Cyanex 302 diluted in kerosene at A:O ratio of 1:1. These are shown in Fig. 4 alongside with the corresponding isotherms at 25 °C for comparison. Generally, the extraction of cadmium increases slightly as the temperature increases from

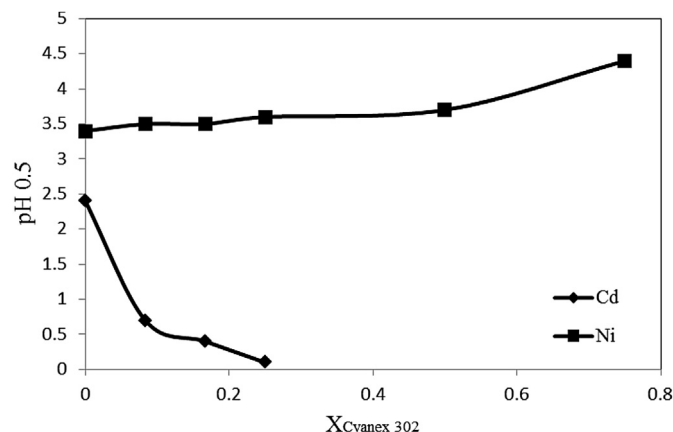


Fig. 3. Effect of adding Cyanex 302 on $pH_{0.5}$.

25 °C to 60 °C; however, temperature had no significant effect on the cadmium extraction at $pH > 1.5$. Similarly, nickel extraction increases by less than 20% with increasing temperature from 25 °C to 60 °C. As both extraction isotherms are shifted more or less to the same extent towards lower pHs by increasing the temperature, it indicates that higher temperatures are not beneficial for the separation of the two metal ions. This is in contrast to the findings reported by Darvishi et al. [18] for extraction of nickel and cobalt using the same mixtures of D2EHPA and Cyanex 302.

3.3. Thermodynamic study

Experimental temperature plays an important role in a liquid–liquid extraction process. The influence of temperature has been studied in the present work for cadmium extraction at pH 2 and fixed concentrations of D2EHPA and Cyanex 302 (D2EHPA = 0.5 M, Cyanex 302 = 0.1 M) in a synergistic system. If the relationship between distribution ratio and temperature is obtained, the change of enthalpy of the reaction, ΔH , can be calculated according to the following:

$$\frac{\Delta D}{\Delta(1/T)} = \frac{-\Delta H}{2.303R} \quad (3)$$

Table 3

Values of D_{Cd} , D_{Ni} and $\beta_{Cd/Ni}$ for different mixtures of D2EHPA with Cyanex 302.

Molar ratio of D2EHPA: Cyanex 302		pH			
		2	2.5	3	3.5
0.6:0.0	D_{Cd}	0.116	1.428	7.467	18.646
	D_{Ni}	0.245	0.322	0.559	1.157
	$\beta_{Cd/Ni}$	4.70×10^{-1}	4.43×10	1.33×10	1.61×10
0.55:0.05	D_{Cd}	14.528	46.393	116.647	343.828
	D_{Ni}	0.219	0.294	0.485	1.094
	$\beta_{Cd/Ni}$	6.63×10	1.58×10^2	2.40×10^2	3.14×10^2
0.5:0.1	D_{Cd}	26.322	71.993	187.679	665.667
	D_{Ni}	0.203	0.261	0.399	0.989
	$\beta_{Cd/Ni}$	1.30×10^2	2.76×10^2	4.70×10^2	6.73×10^2
0.45:0.15	D_{Cd}	713.286	1999	3332.333	9999
	D_{Ni}	0.192	0.246	0.389	0.818
	$\beta_{Cd/Ni}$	3.71×10^3	8.13×10^3	8.57×10^3	1.22×10^4
0.3:0.3	D_{Cd}	768.231	4999	9999	—
	D_{Ni}	0.185	0.224	0.329	0.739
	$\beta_{Cd/Ni}$	4.15×10^3	2.23×10^4	3.04×10^4	—
0.15:0.45	D_{Cd}	9999	9999	9999	—
	D_{Ni}	0.0353	0.0466	0.0810	0.270
	$\beta_{Cd/Ni}$	2.83×10^5	2.15×10^5	1.23×10^5	—

Table 4
Synergistic enhancement coefficient of Cd and Ni for different mixtures of D2EHPA with Cyanex 302.

Molar ratio of D2EHPA: Cyanex 302		pH		
		2	2.5	3
0.45:0.15	$D_1 + D_2$ Cd	9999.10	10000.08	9999.02
	$D_1 + D_2$ Ni	0.22	0.31	0.45
	D_{mix} Cd	713.286	1999	3332.333
	D_{mix} Ni	0.192	0.246	0.389
	R Cd	0.071	0.199	0.333
	R Ni	0.880	0.786	0.772
0.3:0.3	$D_1 + D_2$ Cd	9999.086	9999.26	10000.57
	$D_1 + D_2$ Ni	0.210	0.280	0.411
	D_{mix} Cd	768.231	4999	9999
	D_{mix} Ni	0.185	0.224	0.329
	R Cd	0.076	0.499	0.999
	R Ni	0.856	0.759	0.743
0.15:0.45	$D_1 + D_2$ Cd	9999.023	9999.12	9999.7
	$D_1 + D_2$ Ni	0.057	0.095	0.168
	D_{mix} Cd	9999	9999	9999
	D_{mix} Ni	0.0353	0.0466	0.0810
	R Cd	0.999	0.999	0.999
	R Ni	0.612	0.487	0.483

The change of Gibbs free energy (ΔG) and the change of entropy (ΔS) can thus be determined by Eqs. (4) and (5), respectively, when T is 298 K.

$$\Delta G = -RT \ln K \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} \quad (5)$$

Plot of $\log D$ versus T^{-1} (K^{-1}) is shown in Fig. 5. The ΔH , ΔG , and ΔS values were calculated as 29.19 kJ mol $^{-1}$, 1.59 kJ mol $^{-1}$, and 92.62 J mol $^{-1}$ K $^{-1}$, respectively. It can be seen that the sign of ΔH is positive, indicating that synergistic extraction process is endothermically driven. The ΔS value is positive, implying that the synergistic extraction may occur easily, which is in accordance with the theory of increasing entropy from the view of statistics.

3.4. Extraction mechanism

3.4.1. Extraction mechanism of cadmium by D2EHPA

In order to determine the formation of metal–organic complex during extraction of cadmium, a dimer state of D2EHPA has been

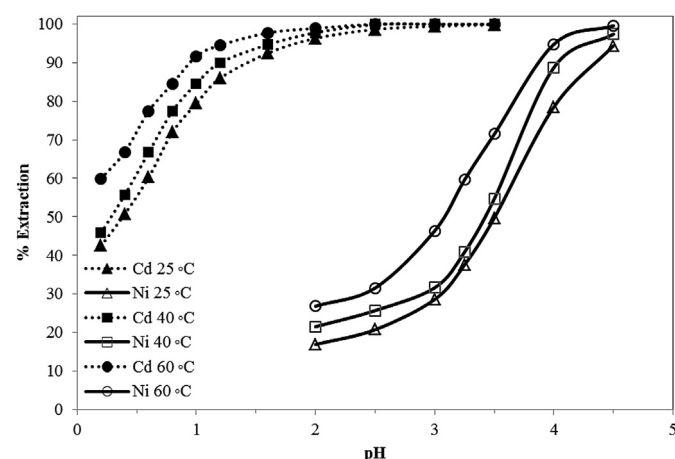


Fig. 4. Effect of temperature on the extraction of cadmium and nickel using 0.5 M D2EHPA and 0.1 M Cyanex 302 and A/O ratio of 1:1.

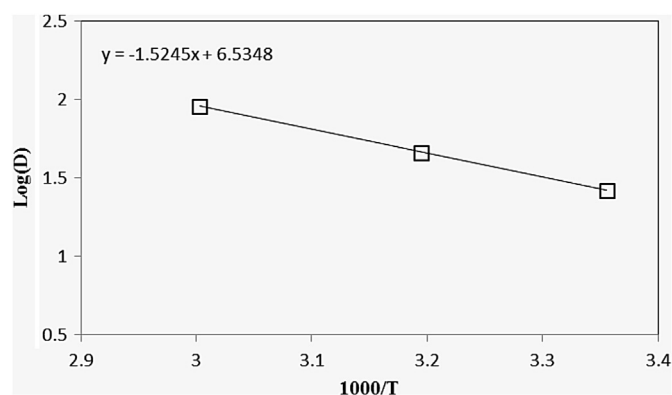
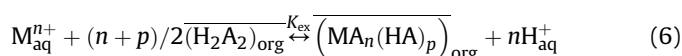


Fig. 5. Relationship between distribution coefficient and temperature, pH = 2.

considered as reported by various authors [26–29]. Assuming that the solubilities of the extractant and the metal–extractant complex in the aqueous phase are negligible and that the species extracted are not associated with each other, the extraction mechanism of the metal ion (in this case cadmium) with D2EHPA in kerosene may be expressed as follows:



Where (H_2A_2) is extractant in dimeric form, M is metal; n is valence of the metal or metal complex ion and p number of molecules of extractant engaged in the reaction. The equilibrium constant of the extraction reaction K_{ex} , can be given as a function of molar concentration, provided that the ionic strength of the aqueous solution is constant.

$$[K_{\text{ex}} = [MA_n(HA)_p]_{\text{org}} [H^+]_{\text{aq}}^n / [M^{n+}]_{\text{aq}} [H_2A_2]_{\text{org}}^{(n+p)/2}] \quad (7)$$

The distribution coefficient, D , can be substituted into the above equation, which gives:

$$D = K_{\text{ex}} [H_2A_2]_{\text{org}}^{(n+p)/2} / [H^+]_{\text{aq}}^n \quad (8)$$

By taking the logarithm of Eq. (8):

$$\log D = \log K_{\text{ex}} + (n+p)/2 \log [H_2A_2]_{\text{org}} + n \text{ pH} \quad (9)$$

If the metal complex is not formed in the aqueous solution and the concentration of the extractant is not changed during the extraction reaction, the plot of $\log D$ against pH yields a linear relationship the slope of which gives the charge on the aqueous metal ion, n . As shown in Fig. 6, for cadmium, the plots of $\log D$ vs. equilibrium pH gave straight lines with a slope of about 2 for sole D2EHPA (0.5 M), suggesting the totally released protons included two molecule of H^+ during extraction. In addition, when the equilibrium pH is not changed during the extraction reaction, the plot of $\log D$ against $\log [H_2A_2]_{\text{org}}$ gives a slope $(n+p)/2$, which the value of p can be determined. In this investigation concentration of D2EHPA was varied in the range 0.15–0.6 (M) in kerosene. Fig. 7, shows a plot of $\log D$ vs. $\log [H_2A_2]_{\text{org}}$ at pH = 3, which indicates that the extraction of cadmium was linearly related to the extractant concentration. The slope value $\{(n+p)/2\}$ was determined to be ~ 1.5 , and assuming the value of 2 for n , the p value becomes 1.

As a result, the mechanism for cadmium extraction by the sole D2EHPA may be represented as:

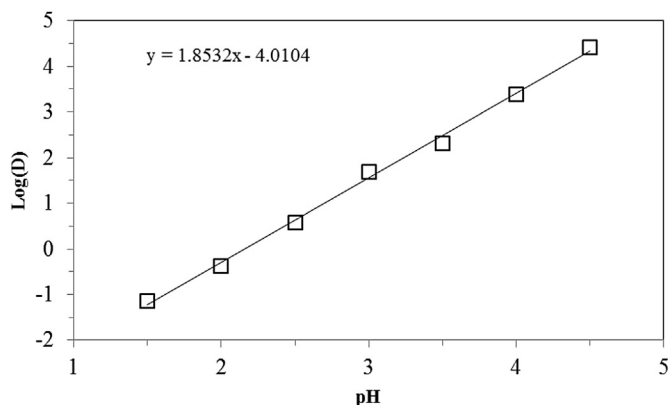
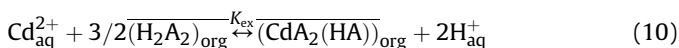


Fig. 6. Effect of pH on the extraction of cadmium with D2EHPA at concentrations of 0.5 M extractant.



It indicates that each cadmium ion is solvated with 1.5 molecule of dimeric D2EHPA with the formation of $(\text{CdA}_2(\text{HA}))_{\text{org}}$ complex in the organic phase. This is in agreement with the findings of Kumar et al. [9].

3.4.2. Extraction mechanism of cadmium by 0.5 M–0.1 M mixture of D2EHPA and Cyanex 302

In a similar manner, a series of experiments were carried out and the conventional slope analysis method was used in order to elucidate the extraction mechanism for the mixed-extractant system. As shown in Fig. 8, the plots of $\log D_m$ versus pH at fixed concentrations of Cyanex 302 (0.1 M) and D2EHPA (0.5 M) give a straight line with a slope of about 1.0, which suggests that there is one released protons in the extraction reaction equation.

Similarly, at fixed aqueous acidity (pH = 3) and concentration of the Cyanex 302 (0.1 M), the plots of $\log D_m$ –pH are linear with slopes of about 1.0 for various concentrations of D2EHPA (Fig. 9). This indicates that one molecule of D2EHPA is involved in the extraction reaction. The extraction mechanism for cadmium extraction may be represented as below, provided that extracted compounds are not associated with each other.

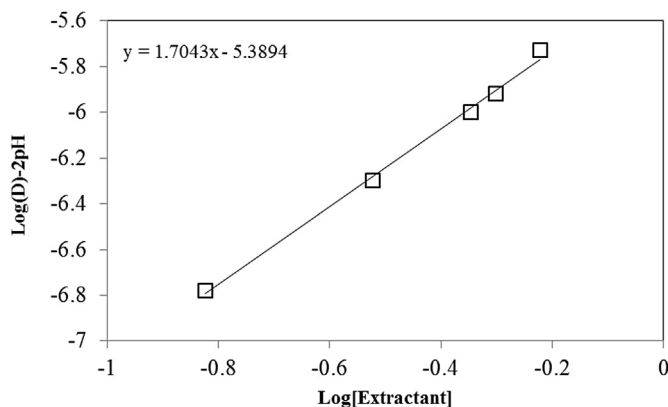
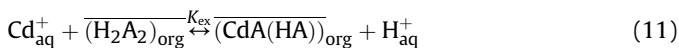


Fig. 7. Effect of D2EHPA concentration on the extraction of cadmium, pH = 3.

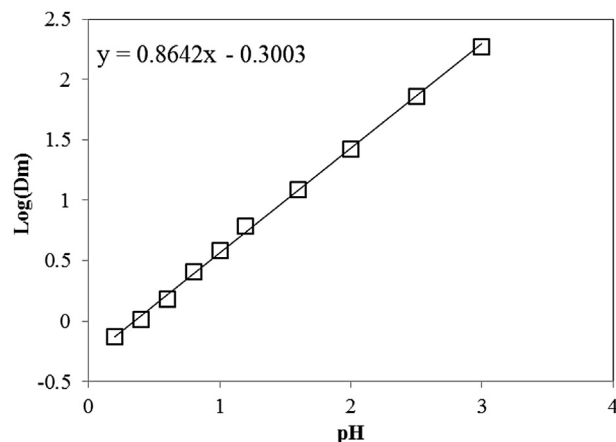


Fig. 8. Effect of pH on the extraction of cadmium by mixtures of D2EHPA and Cyanex 302.

3.5. Distribution coefficient

A general multiple linear equation was used for finding the equation of distribution coefficient for cadmium as a function of temperature (T) and pH independent variables. The coefficients of the equation were calculated via multiple linear regressions. At fixed concentrations of extractants (D2EHPA = 0.5 M, Cyanex 302 = 0.1 M) the insignificant terms were identified by applying the ANOVA technique and eliminated from the equations with not much change in the precision of the correlation. The resulting correlation for distribution coefficient of cadmium is as follows:

$$\log(D_{\text{Cd}}) = -20.65 + 0.038 \times T + 7.32 \times \text{pH} - 1.104 \times \text{pH}^2 \quad (12)$$

A summary of the ANOVA results for the model is tabulated in Table 5. The model F -value of 16 implies that the model is significant. There is only a 0.1% chance that F -value this large could occur due to noise. Values of p (Prob > F) for model terms are less than 0.05 indicating they are considered to be statistically significant. This is desirable as it demonstrates that the terms in the model have a significant effect on the response [30].

Fig. 10 compares the experimental distribution coefficients of cadmium with the model predicted values. It can be seen in this figure that the predicted values from the model are in good agreement with the experimental data. At low pHs, the proposed

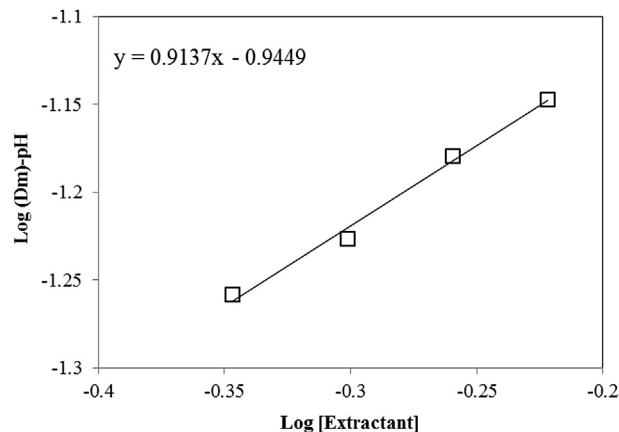


Fig. 9. Effect of D2EHPA concentration on the extraction of cadmium, pH = 3.

Table 5
Analysis of variance table.

Source	Sum of squares	Mean square	df	p-value	F-value	
Model	10.42	3.47	3	0.0010	16	Significant
A-T	3.67	3.67	1	0.0034	16.90	
B-pH	5.84	5.84	1	0.0008	26.90	
B ²	0.91	0.91	1	0.0743	4.21	
Residual	1.74	0.22	8			

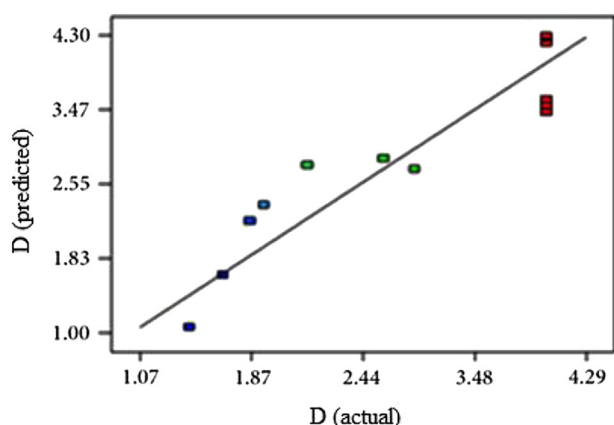


Fig. 10. Comparison of experimental data of distribution coefficient for cadmium with predicted values from the model.

correlation has excellent ability to predict distribution coefficient with an appropriate accuracy while discrepancies at higher pHs can be attributed to the sensitivity of the distribution coefficient to pH in this region. At high pH region (high extraction percentages), distribution coefficient considerably increases while extraction percentage increases only slightly.

4. Conclusions

Mixtures of D2EHPA and Cyanex 302 show evident synergistic effects when applied to extract cadmium and nickel from sulfate solutions. In the presence of the sole D2EHPA, the percentage of extraction for both cadmium and nickel increased with increasing the equilibrium pH. Cadmium extraction with D2EHPA, however, involves co-extraction of nickel. Adding Cyanex 302 to D2EHPA caused a synergistic effect and shifted the extraction curve of cadmium and nickel to the left and right, respectively. As a result, the separation factor and $\Delta pH_{0.5}$ value increased. Increasing the ratio of Cyanex 302 to D2EHPA, improved the cadmium separation from cadmium–nickel solution. Mixture of 0.15 M D2EHPA and 0.45 M Cyanex 302 resulted in the highest separation factor (2.83×10^5) and the largest $\Delta pH_{0.5}$ (>4.4). By increasing the temperature from 25 °C to 60 °C, the percentage of extraction of nickel and cadmium increased slightly. The calculated thermodynamic

parameters, ΔH , ΔG , and ΔS indicate that synergistic extraction reaction of cadmium is endothermically driven. The extraction mechanism and behavior of cadmium by single D2EHPA are different from that of mixtures of D2EHPA and Cyanex 302. The extraction studies showed the formation of $(CdA_2(HA))_{org}$ species in the organic feed with sole D2EHPA and $(CdA(HA))_{org}$ with the 0.5 M:0.1 M mixture of D2EHPA and Cyanex 302. An equation was found via multiple linear regression for estimation of distribution coefficient of cadmium. The distribution coefficients of cadmium calculated based on the obtained correlation are in good agreement with the experimental values.

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